



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS OF HYDROGELS BY FREE RADICAL
COPOLYMERIZATION OF SAGO STARCH OR CHITOSAN AND
HYDROPHILIC VINYL MONOMERS AND THEIR
CHARACTERIZATIONS**

ABDUEL MAJID K. NAJJAR

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By

ABDUEL MAJID K. NAJJAR

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
in Fulfilment of the Requirement for the Degree of Doctor of Philosophy**

June 2002



DEDICATION

To the souls of my beloved father and grandfather in the heavens (Khalifa and Emhemmed), who regretfully did not live to see this work, which resulted from their gift of many years of love, encourage and support to me.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in
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Chairman: Professor Wan Md. Zin Wan Yunus, Ph.D.

Faculty: Science and Environmental Studies

Sago starch was incorporated in the synthesis of polymer gel networks by free radical crosslinking copolymerization in an aqueous solution using potassium persulfate as an initiator. Three different monomers (2-acrylamido-2-methylpropanesulfonic acid (AMPS), acrylic acid and methyl-2-acrylamido-2-methoxyacetate (MAMOA)) with a common crosslinking agent (*N,N'*-methylenebisacrylamide (NMBA)) were used to synthesize these gel networks. A series of studies was carried out to evaluate and optimize the effect of the reaction parameters such as the amount of the monomer, the crosslinking agent and sago starch as well as liquor volume on the polymer gel networks yield. It was found that the percentages of gelation fraction and total conversion were dependent on these parameters.

The swelling behaviors of these polymeric gel networks from the dry state in distilled water and NaCl solutions of different concentration were also investigated. The maximum saturated water absorbency of 440 g H₂O/g dry gel was obtained for the gel network prepared from 1 g sago starch, 38.16×10^{-3} mol AMPS and 1.29×10^{-3} mol NMBA in the presence of 45 mL liquor volume. The absorbency of the hydrogel networks in the salt solutions was affected by the salt concentrations and the charge number of cations and anions.

The swelling capacity of the sago starch-poly(acrylic acid)-poly(NMBA) gel network could be increased by saponification with NaOH solution, and the saponification conditions (treatment temperature, treatment period and concentration of NaOH solution) were important in determining the water absorbency.

Polymeric materials from sago starch, acrylic acid and NMBA were synthesized in cylindrical form to evaluate their potential use as a water soluble drug carrier. The effects of the amount of sago starch, acrylic acid and NMBA during polymerization on the swelling behavior as well as on the loading and releasing of MgSO₄ were investigated. The amount of salt loaded was found to be dependent upon the concentration of MgSO₄ solution. The release profile of MgSO₄ can be controlled by varying the amount of poly(acrylic acid) and the crosslinking density in the gel network.

Preparation of the hydrogels by homogeneous grafting of MAMOA onto sago starch in an aqueous solution using potassium persulfate as an initiator was also investigated. The effects of the reaction conditions have been studied in term of percentage of grafting (% *G*). The optimum polymerization temperature and reaction period were found to be 50 °C and 2 hr, respectively. The % *G* was increased with the increase of the amount of monomer but decreased with the increase of amount of sago starch. The highest % *G* of about 62 % was obtained when the copolymerization reaction was carried out for 2 hr at 50 °C using 0.74×10^{-3} mol of potassium persulfate and 11.55×10^{-3} mol of MAMOA with 2 g of sago starch in 35 mL distilled water.

2-Acrylamido-2-methylpropanesulfonic acid (AMPS) has also been successfully grafted onto chitosan from homogenous solution using potassium persulfate as a redox initiator. The maximum percentage of grafting was about 180% under the optimum conditions (1% V/V acetic acid, 50 °C reaction temperature, 10 min chitosan-potassium persulfate mixing period, 0.37×10^{-3} mol of potassium persulfate and 28.96×10^{-3} mol of AMPS). The grafted chitosan was insoluble in the acid solution used for the grafting.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi syarat untuk mendapatkan ijazah Doktor Falsafah

**SINTESIS HIDROGEL MELALUI PENGKOPOLIMERAN RADIKAL
BEBAS KANJI SAGU ATAU KITOSAN DAN MONOMER VINIL
HIDROFILIK DAN PENCIRIANNYA**

Oleh

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Kanji sagu telah digunakan dalam penyediaan polimer rangkaian hidrogel secara pempolimeran radikal bebas dalam larutan akueus menggunakan kalium persulfat sebagai pemula. Tiga monomer yang berbeza (asid-2-akrilamido-2-metilpropanasulfonik (AMPS), asid akrilik dan metil-2-akrilamido-2-metoksiasetat (MAMOA) dengan agen perangkai silang (N,N'-metilenabisakrilamida (NMBA)) digunakan untuk menyedia rangkaian gel tersebut. Kajian secara sistematik telah dilakukan bagi menentukan keadaan optimum yang mempengaruhi tindak balas pempolimeran seperti kuantiti monomer, agen perangkai silang dan kanji sagu serta pelarut terhadap hasil polimer rangkaian hidrogel. Didapati peratus pengelatinan dan peratus petukaran total bergantung kepada parameter ini.

Perlakuan pengembangan rangkaian gel yang kering dikaji dalam air dan juga larutan NaCl dengan kepekatan yang berbeza. Didapati penyerapan tepu air

maksima adalah 440 g air/ g gel kering bagi gel kering yang disediakan daripada 1.00 g kanji sagu, 38.16×10^{-3} mol dan 1.29×10^{-3} mol NMBA dalam 45 mL pelarut. Kesan terhadap kepekatan, cas kation dan cas anion terhadap penyerapan rangkaian hidrogel dalam salin juga dikaji. Penyerapan rangkaian hidrogel dalam larutan garam bergantung kepada kepekatan garam serta cas kation dan cas anion.

Kapasiti pengembangan rangkaian gel kanji sagu-poli(asid akrilik)-poli (NMBA) boleh ditingkatkan melalui disaponikasikan dengan larutan NaOH. Kesan terhadap keadaan saponikasi (suhu rawatan, masa rawatan dan kepekatan larutan NaOH) amat penting bagi menentukan penyerapan air.

Bahan polimer dari kanji sagu, asid akrilik dan NMBA disintesis dalam bentuk selinder unjuk kajian penggunaannya sebagai bahan pembawa dadah larut-air. Kesan kuantiti kanji sagu, asid akrilik dan NMBA semasa pempolimeran terhadap perlakuan pengembangan serta pemuatan dan pembebasan MgSO_4 juga dikaji. Akaun garam yang dapat dimuatkan didapati bergantung kepada larutan MgSO_4 . Profil pelepasan MgSO_4 dapat dikawal dengan mengubah akaun poli(asid akrilik) dan ketumpatan rangkai silang dalam rangkaian hidrogel.

Kajian ini juga melibatkan penyediaan hidrogel secara pencangkukan homogen metil-2-akrilamido-2-metoksiasetat (MAMOA) ke atas kanji sagu dalam larutan akueus menggunakan kalium persulfat sebagai pemula. Kesan terhadap keadaan tindak balas dikaji berdasarkan peratus cangkukan (% G). Suhu optimum bagi pempolimeran dan masa tindak balas masing-masing adalah 50 °C dan 2

jam. Peratus cangkukan bertambah dengan pertambahan amaun monomer tetapi berkurang dengan pertambahan amaun kanji sagu. Peratus cangkukan maksima adalah 62% apabila tindak balas pengkopolimeran dilakukan selama 2 jam pada suhu 50 °C menggunakan 0.74×10^{-3} mol kalium persulfat, 11.55×10^{-3} mol MAMOA dengan 2 g kanji sagu dan 35 mL air suling.

Asid 2-akrilamido-2-metipropanasulfonik (AMPS) juga berjaya dicangkukkan ke atas kitosan dalam larutan homogen menggunakan kalium persulfat sebagai pemula redoks. Peratus cangkukan maksima adalah 180% pada keadaan optimum (1% V/V asid asetik, suhu tindak balas 50°C, masa campuran kitosan dengan kalium persulfat 10 min, kuantiti kalium persulfat 0.37×10^{-3} mol dan kuantiti AMPS 28.96×10^{-3} mol). Kitosan yang dicangkukkan tidak larut dalam larutan asid yang diguna untuk pengcangkukan.

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I certify that an Examination Committee met on 14th June 2002 to conduct the final examination of Abduel Majid K. Najjar on his Doctor of Philosophy thesis entitled “Synthesis of Hydrogels by Free radical Copolymerization of Sago Starch or Chitosan and Hydrophilic Vinyl Monomers and Their Characterizations” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



ABDUEL MAJID K. NAJJAR

Date: 31/07/2002

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